Coverage Effect of the CO₂ Adsorption Mechanisms on CeO₂(111) by First Principles Analysis

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Coverage effect of the CO₂ adsorption mechanisms on CeO₂(111) by first principles analysis

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ABSTRACT

The adsorption of carbon dioxide on $\text{CeO}_2(111)$ has been studied using density functional theory. At low coverage ($1/9$ monolayer), CO_2 is found to preferably adsorb in a monodentate configuration forming a carbonate species with a surface O atom. In this configuration, the CO_2 molecule is bent with a O-C-O angle of 129° and a remarkable elongation (to $1.27 \text{ \AA}$) of the C-O bond length compared to the gas phase molecule, indicating a high degree of CO_2 activation. A similar activation is observed when the CO_2 molecule adsorbs as bidentate carbonate, however, this configuration is less stable. Linear configurations are found to adsorb very weakly at low coverage by physisorption. Increasing the coverage leads to a decrease of the stability of mono- and bidentate configurations which can be attributed to repulsive interactions between adjacent adsorbates and the limited capacity of the $\text{CeO}_2(111)$ surface to donate electrons to the adsorbates. In contrast, the binding energy of linearly adsorbed CO_2 is shown to be coverage independent. At coverages $>1/4$ monolayer, we have also addressed the stability of mixed configurations where mono-, bidentate and linear species are present simultaneously on the surface. The most stable configurations are observed when $1/3$ monolayer CO_2 is bound as monodentate species and additional molecules are physisorbed linearly. Analysis of the projected density of states has revealed that the orbitals of linear species in the first partial layer on top of monodentate ones are shifted to lower energies compared to the second partial layer suggesting stabilization of the former. These findings provide fundamental insight into the CO_2 adsorption mechanism on CeO_2 and potentially assist the design of new Ce-based materials for CO_2 catalysis.

INTRODUCTION

Rare earth metal oxides such as CeO₂, La₂O₃, Yb₂O₃ and Lu₂O₃ are highly interesting materials for a wide range of applications, for example as gate insulators^{1,2}, abrasive materials^{3,4}, catalysts in automotives⁵ or for syngas production⁶. The most interesting and studied metal oxide among these is ceria. Due to its potential to store and release oxygen depending on the process conditions it is a superior catalyst for CO oxidation and NO_x reduction reaction^{5,7,8} but also for hydrogenation of CO₂^{9,10}.

Hydrocarbon production from CO₂ is in particular interesting since it provides high energy density fuel from CO₂ which is omnipresent in our environment. The dominating mechanism for this process is the Sabatier reaction (I). The reaction itself is exothermic. However, remarkable activation barriers are present due to the high thermodynamic stability of CO₂¹². The activation

barriers can be decreased when the linear CO₂ molecule transforms into a bent configuration prior to the hydrogenation reaction. The bent CO₂⁻ is ca. 0.5 eV¹² less stable than the linear molecule facilitating subsequent reactions such as CO₂ dissociation or hydrogenation.

Numerous studies have been conducted on the adsorption and activation of CO₂ on metal surfaces such as Cu¹³⁻¹⁶, Pt^{17,18}, Pd^{19,20} and Fe^{16,21,22} where the Fe(110) surface has been identified to be most suitable for CO₂ activation²³. This has been attributed to the elongation of one of the C-O bonds (to ca. 1.30 Å) and a remarkable charge transfer (0.83 e⁻) from the surface to the CO₂ molecule.²³ The most widely used metals for CO₂ methanation, however, are Ni and Rh.¹¹ Using DFT calculations, it has been verified, that the reaction on Ni involves the formation of the bent CO₂ intermediate.²⁴

Density functional theory (DFT) calculations of the adsorption mechanism on metal oxides have revealed that CO₂ adsorbs preferably in a linear configuration on most monoxides such as TiO, CrO, VO and MnO.²⁵ The same behavior has been observed on TiO₂^{26,27} and LaMnO₃²⁸. In contrast, favorable bent geometries were determined on CaO and FeO.²⁵ The different adsorption mechanisms can be attributed to the acidity of the metal oxide surface.^{29,30} In this scheme, a molecule adsorbing on the metal oxide surface is regarded as Lewis base when reacting on the metal cation and as Lewis acid when reacting on the O²⁻ site. Most metal oxide surfaces react as Lewis acids on which organic molecules are adsorbed without dissociation. Basic metal oxides, on the other hand, rather lead to dissociation of organic molecules and, in the case of CO₂, promote the formation of a bent CO₂⁻ species including a charge transfer from O₂⁻ sites to the CO₂ species.

In experimental studies using IR and X-ray photoelectron spectroscopy the presence of bent carbonate species on CeO₂ upon CO₂ adsorption has been observed³¹ suggesting the CeO₂ surface to react as Lewis base in the CO₂ adsorption process. Theoretical evidence from DFT calculations on the adsorption processes on CeO₂, however, is rare. This is mainly due to the complex electronic structure of CeO₂ exhibiting highly localized 4f states about 3 eV above the valence band.^{32,33} Upon reduction of Ce⁴⁺ to Ce³⁺ these states become occupied³⁴⁻³⁶ and an accurate description of the electronic structure with standard DFT gets problematic³⁷. Nevertheless, standard DFT calculations have shown to correctly describe the stoichiometric CeO₂ bulk and surface³⁷⁻³⁹ as long as no reduction of Ce⁴⁺ to Ce³⁺ is involved. In fact, comparing standard DFT with DFT+U calculations it has been shown that even CO adsorption on the (111) and (110) surface can be accurately treated with standard DFT.⁷ Results of both standard DFT and DFT+U methods were in reasonable agreement with experimental studies.^{40,41} While CO

physisorbed on the (111) surface, a carbonate species with two adjacent surface O atoms was formed when adsorbed on the (110) surface.⁷ Calculations based on the DFT+U method have been applied recently for the investigation of CO₂ adsorption on stoichiometric and reduced CeO₂(110) showing the formation of a bent CO₂ species on the reduced surface.⁴² Only weak adsorption without geometric deformation has been observed on the stoichiometric surface.⁴²

In this study, CO₂ adsorption has been investigated on the CeO₂(111) surface using standard DFT calculations. Different adsorption mechanisms are examined for CO₂ molecules at coverages ranging from 1/9 to 1 monolayer (ML). The coverage effect for the most stable configurations is discussed in terms of stability, geometry and electronic structure. The results are further compared to CO₂ adsorption on other metal and metal oxide surfaces giving an estimate of the degree of CO₂ activation. Selected adsorption modes are additionally simulated using hybrid functional (PBE0⁴³) calculations and compared to the results of standard DFT verifying the qualitative accuracy of the latter.

THEORETICAL METHODS

The calculations of this study are based on DFT and are carried out with the Quickstep⁴⁴ module of the CP2K program package, a suite of programs developed for efficient electronic structure calculations and molecular dynamics based on the Gaussian and plane waves formalism⁴⁵. Valence electrons are treated explicitly whereas interactions with the frozen atom core are described with norm-conserving pseudopotentials.⁴⁶ Here, 4, 6 and 12 electrons are explicitly considered in the valence shell for C, O and Ce atoms, respectively. A triple-zeta valence plus polarization (TZV2P) basis set, optimized according to the Mol-Opt method⁴⁷, is adopted for C and O atoms. The basis set for Ce is optimized with the atomic ground state⁴⁵ and has the form of a double-zeta valence (DZV) basis set without polarization. For auxiliary plane wave expansion of the charge density, the energy cutoff is set to 1000 Ry. Exchange-correlation potentials are modeled within the general gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional.⁴⁸ The GGA formalism has been shown to yield reasonably accurate results for the CeO₂ bulk³⁷ and its (111) surface^{38,39}. To confirm the suitability of the standard DFT method for the simulation of CO₂ adsorption on CeO₂(111), selected configurations were additionally calculated ~~hybrid functional calculations are conducted for selected configurations~~ using the PBE⁴³ hybrid functional with 20% exact exchange and DFT+U calculations with the PBE functional and a U value of 5 eV. Some configurations are further optimized introducing a Grimme D2⁴⁹ potential to account for van der Waals interactions between adsorbates and surface slab. It has been verified that 15 Å are sufficient to eliminate effects of the van der Waals interactions on the binding energy. All calculations are performed with periodic boundary conditions.

The size of the simulated supercell is a critical parameter in real space calculations. It defines the accuracy of the physical properties of the system and the computational time frame needed. The supercell size has been optimized to reach convergence of the bulk properties such as lattice parameter and total energy per CeO₂ unit. A supercell containing 81 atoms has been found to be sufficient for the evaluated bulk properties. In this supercell, the primitive unit cell of fluorite CeO₂ is repeated three times in all spatial directions. The optimized lattice parameter for this set-up resulted in 5.48 Å which is in good agreement with previous calculations (5.47 Å)³⁷ and experiments (5.41 Å)⁵⁰ (Table 1). The (111) surface is realized by introducing a vacuum of 15 Å along the [111] direction to avoid interaction with the periodic images of the slab. Convergence of the surface energy within 0.02 J/m² with respect to the slab thickness is reached with six O-Ce-O trilayers. In a p(3x3) expansion of the (111) surface unit cell, the surface energy is calculated to be 0.74 J/m² in excellent agreement with previous calculations using the DFT+U method (0.72 J/m²)⁵¹ (Table 1). The band gap between the O-2p and Ce-4f states of the clean CeO₂(111) slab is calculated to be 1.99 eV, which is again in good agreement with previous calculations using the PBE exchange-correlation functional (2 eV)³⁷.

Depending on the CO₂ coverage, different surface dimensions are used: slabs with p(3x3), p(4x3) and p(4x4) expansions of the surface unit cell corresponding to a total of 9, 12 and 16 active Ce-sites, respectively. In all cases, the slab consists of six trilayers of which the top three are allowed to relax while the three bottom trilayers were fixed to simulate the bulk properties. Adsorption of CO₂ was simulated on one exposed surface. The CO₂ binding energies (E_B) is calculated according to:

$$E_B = \frac{E_{\text{slab}+n\text{CO}_2} - (E_{\text{slab}} + n \cdot E_{\text{CO}_2,\text{g}})}{n}, \quad (\text{II})$$

where n is the number of adsorbed species on the described surface and $E_{\text{slab}+n\text{CO}_2}$ denotes the energy of the surface slab plus n adsorbates. Equation (II) implies that negative values for E_B indicate exothermic desorption processes. The energy of an isolated CO_2 molecule ($E_{\text{CO}_2,\text{g}}$) is calculated in a periodically repeated cell of $15 \times 15 \times 15 \text{ \AA}$. Optimization of the geometry of the CO_2 molecule in gas phase resulted in a O-C-O angle (α_{OCO}) of 180° and a C=O bond length ($d_{\text{C-O}}$) of $1.17 \text{ \AA}$ in good agreement with experiments ($1.16 \text{ \AA}$)⁵² (Table 2). Geometrical properties of adsorbed CO_2 are characterized by α_{OCO} , the C-O bond length ($d_{\text{C-O}}$ or $d_{\text{C-O1}}$ and $d_{\text{C-O2}}$) and the adsorption height which is indicated by the distance of C to the closest surface O atom ($d_{\text{C-Osurf}}$) for carbonate species and by the height of C above the first layer of Ce (Δz_{CO_2}) for linear species (Figure 1).

Mulliken population analysis⁵³ is used to determine the charge transfer between surface and adsorbate. Further analysis of the electronic structure is carried out by projection of the Kohn-Sham orbitals at single atoms (projected density of states, PDOS) and the summation of the projections at the relevant atoms when multi-atomic groups are of interest such as the CO_2 molecule or selected slab atoms. In this respect, the PDOS denoted as “total” as in Figure 2 and Figure 9 corresponds to the summation of the projections at all atoms of the system. The DOS is shifted so that the upper edge of the valence band of the $\text{CeO}_2(111)$ slab is positioned at 0 eV.

RESULTS AND DISCUSSION

Adsorption Mechanisms of Isolated CO₂ (1/9 ML). *Stability and Geometry.* The adsorption mechanism of isolated CO₂ is simulated on a CeO₂(111) slab with a p(3x3) surface unit cell at a CO₂ coverage of 1/9 ML. At this coverage, it is expected that interactions between adsorbates are negligible and the adsorbed species can be assumed to be isolated. Optimization of the geometry leads to three stable configurations: i) mono- (Figure 1a,d) and ii) bidentate (Figure 1b,e) carbonate species in a bent conformation and iii) linearly adsorbed CO₂ (Figure 1c,f). The monodentate bent CO₂ forms spontaneously from a linear configuration located 1.7 Å above the surface indicating that no activation energy is required for the formation of the bent CO₂ molecule (see Figure S1 for initial configurations of all stable species). However, using nudge elastic band (NEB) calculations, an energy barrier of 0.2 eV is observed for the transition from the linear to the monodentate configuration (Figure S2). Geometric properties of the transition state can be found in the Supporting Information (Figure S2). Among the calculated configurations these, the monodentate species configuration is most stable with a binding energy of -0.31 eV, followed by the bidentate one with E_B = -0.12 eV. Both mono- and bidentate configurations are additionally optimized with PBE0 calculations resulting in a binding energy of -0.68 eV and -0.42 eV, respectively (Table 2, Figure S34). The lower values of the binding energy indicate stronger binding compared to standard DFT calculations. Using the DFT+U approach, binding energies are determined to be -0.28 and -0.04 eV for the mono- and bidentate species, respectively, and thus reasonably close to the PBE results (Table 2, Figure S3). Results of the two methods are in qualitative agreement with the monodentate species being more stable than the bidentate one and it can be concluded that the results obtained with standard DFT calculations are qualitatively correct. Moreover, no reduced cerium ions are involved in the CO₂

adsorption on stoichiometric CeO₂(111) additionally justifying the use of standard DFT calculations.

Remarkable conformational changes are observed in the bent configurations compared to the linear CO₂ molecule in gas phase (Table 2). In the mono- and bidentate configuration, α_{OCO} decreases remarkably to 130° and 129° (Table 2), respectively. At the same time, both C-O bonds elongate to 1.27 Å in the monodentate configuration which is close to the literature value of a regular C=O bond of carbonyl (1.23-1.26 Å)⁵⁴. Asymmetric bond elongation is observed in the bidentate configuration with 1.22 Å for $d_{\text{C-O1}}$ and 1.30 Å for $d_{\text{C-O2}}$ (see Figure 1 for definition of geometrical quantities). Both distances are in the range of a (partial) double C-O bond. Due to the longer $d_{\text{C-O2}}$, we suggest that, in this case, separation of one O atom is facilitated.

Previously, it has been shown that CO₂ adsorption on pure metal surfaces is only stable and highly activated in the case of Fe²³, whereas endothermic binding energies have been determined for various other metals such as Ni, Rh, Co and Pd²³. The exothermic binding energies found here for mono- and bidentate configurations indicate that the CO₂ bond strength on CeO₂ is comparable to the one on Fe(110). Furthermore, the geometry of the monodentate configuration is similar to the most stable one found on a Ni(110) surface.⁵⁵ In contrast to metal surfaces, most metal oxides such as TiO₂⁵⁶, TiO, ScO and MnO²⁵ favor a linear CO₂ adsorption over the formation of bent mono- or bidentate species. Different behavior has only been shown on FeO where monodentate adsorption and on CaO where bidentate adsorption is favored.²⁵ It is thus suggested, that CeO₂ induces catalytic reaction mechanisms similar to the latter materials.

The distance of C ($d_{\text{C-Osurf}}$) to the closest surface O atom (O_{surf}) in the monodentate configuration is found to be 1.38 Å indicating a partial double bond between the C atom and the

surface O atom. For bidentate species it is 1.41 Å, thereby somewhat larger and corresponding to a single C-O bond. This explains its weaker bond strength.

Computational investigation of CO adsorption on CeO₂(110)⁷ has revealed bond characteristics comparable to the one found here for the monodentate configuration. There, carbon monoxide has been shown to form a carbonate species with two surface O atoms, where the bond length between the C atom and the O atoms of the surface has been determined to be 1.35 Å.⁷

Geometrical properties obtained with PBE0 are represented in Table 2. Using hybrid functional calculations the bond lengths tend to be smaller compared to PBE results. However, in general, only marginal deviations are observed between the different methods.

Adsorption of linear CO₂ (Figure 1c,f) is endothermic with a binding energy of +0.02 eV. This result is obtained without consideration of dispersion interactions. Introducing a D2 Grimme-potential⁴⁹ to account for van der Waals interactions, the binding energy of the reoptimized linear configuration is found to be -0.07 eV indicating the adsorption of linear CO₂ to be exothermic. Hardly any changes in geometry compared to the gas phase CO₂ molecule are observed for the linear configuration. For the simulation without D2, the O-C-O angle decreases slightly to 177.6° whereas $d_{\text{C-O}}$ remains at 1.17 Å for both C-O bonds. The height of the molecule above the surface (Δz_{CO_2} , Figure 1c) is 3.52 Å (Table 2). These results indicate weak interactions between the linear CO₂ molecule and the CeO₂(111) surface.

Electronic Structure. A significant charge transfer from the CeO₂ surface to the CO₂ group was observed in both carbonate configurations resulting in a total charge of -0.46 and -0.40 for the mono- and bidentate species, respectively (Table 2). This is comparable to the charge transfer observed from Pd and Cu surfaces to CO₂²³ and is an indication of the basic character of the CeO₂ surface²⁹. On various other metal oxides such as TiO₂⁵⁶, TiO, ScO and MnO²⁵ a different

behavior has been observed. Linear adsorption has been found to be favored demonstrating an acidic character of these surfaces. Similar behavior is observed here in the case of linear adsorption of CO₂ on CeO₂(111) where the CO₂ molecule has a minor positive charge (+0.03). In other words, depending on the adsorption mechanism, the CeO₂(111) surface can act both as Lewis base or weak acid, however, its basic character is predominant.

Further analysis has been done on the DOS, shown in Figure 2 for monodentate adsorption. The adsorption leads to the evolution of one additional state at the top of the valence band attributed to hybridization of the p-type orbitals of the surface O atom with the orbitals of the CO₂ molecule (see Figure S42 for further details). In the monodentate configuration, this state is located 0.33 eV above the valence band (Figure 2). This was confirmed by PBE0 calculations where this state was found 0.21 eV above the valence band (Figure S5). In general, the DOS obtained with the PBE0 method is similar to the one with PBE (see Figure S5). However, the binding orbital between C and O_{surf} found about 6 eV below the valence band are shifted by 0.67 eV to lower energies. Furthermore, the split between binding and anti-binding CO₂ orbitals is enlarged using the PBE0 method. This explains the lower binding energy that was found with PBE0 for the monodentate configuration.

-Upon formation of a bidentate species, it is found at higher energy (0.62 eV above the valence band, Figure S63) rationalizing the weaker bond of bidentate CO₂ on the CeO₂(111) surface. The evolution of additional CO₂ states above the CeO₂ valence band has been reported previously as well for the adsorption of CO on CeO₂(110).⁷ In the latter case, the additional states are formed 0.3 eV above the valence band.

The acidic nature of the bent CO₂ molecule has been described previously¹² and it promotes the basicity of the CeO₂ surface. Bending of the CO₂ molecule leads to splitting of the

unoccupied Π_u orbital of the linear CO_2 molecule holding $C_{2\infty}$ symmetry into two orbitals, one of which is found at remarkably lower energy.¹² This favors the transfer of substrate electrons to the CO_2 molecule accompanied by the occupation of this orbital. The DOS of gas phase CO_2 and adsorbed species obtained from our calculations confirm this behavior (Figure 3). Upon bending, the HOMO of the linear CO_2 molecule splits into two distinguishable orbitals at slightly different energies (Figure 3). The same is true for the LUMO. Here, the splitting results in a significant shift of one of the non-degenerate orbitals to lower energies (Figure 3a, state 2). HOMO and LUMO of the bent gas phase CO_2 are shown in Figure 3b. When CO_2 is adsorbed on $\text{CeO}_2(111)$ as either of the bent species, the shape of HOMO is similar to the one of the gas phase (Figure 3b). However, several states of the valence band resemble the shape of the LUMO of CO_2 and can be attributed to hybridized carbonate states.

Furthermore, the PDOS of the adsorbed CO_2 species shows a shift of the orbitals of the bidentate species by 0.29 eV to higher energies compared to the monodentate species (Figure 3). This value is in line with the difference in binding energy of the two adsorption mechanisms indicating that it is the major driving force for the higher stability of the monodentate species. The bonding mechanism of the two species, however, is identical.

It has been proposed previously that charge transfer to the bent CO_2 molecule and thus formation of an anionic species leads to the occupation of the hybridized LUMO.¹² The resulting orbitals have bonding character between C and O_{surf} and anti-bonding character between C and the O atoms of the molecule. The anti-bonding character leads to the elongation of the intramolecular C-O bonds which has been found for both mono- and bidentate species and is responsible for the activation of the CO_2 molecule.²³

Bond formation between O_{surf} and C is additionally confirmed by the charge density difference shown in Figure 4. Yellow lobes represent excess of electrons which are mainly found between O_{surf} and C and suggest the occupation of the LUMO of the bent gas phase CO_2 (Figure 3b, state 2). This is further supported by the electron excess around the O atoms of the CO_2 molecule, which resembles the shape of the gas phase LUMO. On Ni(110), being one of the best metal-based catalysts for CO_2 methanation, similar bond characteristics between CO_2 and the surface have been reported based on charge density differences for CO_2 on Ni(110).²⁴ suggesting similar CO_2 reaction mechanisms on $\text{CeO}_2(111)$ and Ni(110). This demonstrates comparable chemical interaction of Ni and CeO_2 with CO_2 and it is thus proposed that mechanisms and properties of reactions involving CO_2 are similar on these surfaces.

The charge density difference of the bidentate species observed between O_{surf} and C (Figure 4b) is equivalent to the one of the monodentate species (Figure 4a). Additionally, the electron excess around the O2 atom is shifted towards the interacting surface Ce atom (Ce_{surf}) indicating polarization of O2 and Ce_{surf} orbitals. However, no chemical bond between O2 and Ce_{surf} is evident from the charge density difference.

In contrast to the bent CO_2 species, the partial DOS of the linearly adsorbed CO_2 is identical to the one of the free molecule lacking any indication of hybridization of the surface orbitals (Figure S63). Thus it can be concluded that the linearly adsorbed molecule does not form chemical bonds and does not cause any perturbation to the surface.

Coverage Effect on Single-Phase Adsorption Mechanisms. Stability and Geometry. In addition to the investigation of mechanisms of isolated CO_2 at 1/9 ML, adsorption is simulated at higher coverages (1/4, 1/3, 1/2, 2/3, 1 ML) in the mono-, bidentate and linear configuration. The resulting binding energies as a function of the CO_2 coverage are shown in Figure 5a. No

coverage effect is observed when CO₂ is exclusively physisorbed in a linear configuration. The binding energy is between 0.0 and +0.05 eV for all calculated coverages (1/9-1 ML). The intramolecular geometry of linear CO₂ is not affected by the coverage. However, an increase of the average distance (Δz_{CO_2}) from the surface (Table 2) is noticeable with increasing coverage from 1/2 (3.43 Å) to 1 ML (3.92 Å), which can be attributed to repulsive interactions between adsorbates and the formation of a second partial layer of linear CO₂.

In contrast to linearly adsorbed CO₂, a significant influence of the coverage on the binding energy is observed for both carbonate configurations. The bond strength for monodentate species decreases monotonously from $E_B = -0.31$ to +0.36 eV with increasing coverage from 1/9 to 2/3 ML. This is, similar to the case of linear adsorption, an indication of repulsive interactions between the adsorbates. In fact, no stable configuration for monodentate species at 1 ML is found. Relaxing the geometry of such a configuration results in a mixed state with linear CO₂ and carbonate species. The change in binding energy of the monodentate configuration is nearly linearly dependent on the coverage up to 1/2 ML ($E_B = -0.08$ eV) followed by a remarkable increase (loss of bond strength) at 2/3 ML ($E_B = +0.36$ eV) (Figure 7). The diminishing bond strength is accompanied by notable changes in the geometry of the configurations, especially at high coverages. This is in particular observable in the monodentate configuration at 2/3 ML due to the oversaturation of Ce surface sites. In the stable monodentate configuration CO₂ interacts with two Ce surface atoms (Figure 1d). Thus, all active sites are occupied already at a coverage of 1/2 ML resulting in a rotation of adsorbed CO₂ away from the corporate surface Ce atom at 2/3 ML (Figure 6a,d) and a drastic decrease in bond strength (increase of E_B , Figure 5a). Furthermore, the distance between the C atom ($\text{Ce}_{\text{surf},2}$) and O_{surf} ($d_{\text{C-Osurf}}$) of monodentate species increases from 1.38 (1/3 ML) to 1.41 Å (2/3 ML) (Figure 5b). No change in $d_{\text{C-Osurf}}$ is observed

at lower coverages. Thus, we conclude that no interactions between adjacent adsorbates are present at coverages $<1/3$ ML.

Similar trends are observed in binding energy and geometry of the bidentate species. Here, E_B increases linearly from -0.12 to +0.71 eV with increasing coverage from $1/9$ to 1 ML indicating a loss in bond strength at high coverages. Caused by repulsive interactions between adsorbates this leads to a change from exothermic to endothermic adsorption between $1/3$ and $1/2$ ML coverage (Figure 5a). Bidentate species interact only with one Ce surface atom which implicates saturation of active sites not until 1 ML coverage and allows for a stable configuration even at 1 ML (Figure 6b,e). In the bidentate configuration, $d_{C-O_{surf}}$ increases only marginally up to $1/3$ ML (1.41-1.42 Å) followed by a remarkable increase to 1.48 Å at 1 ML. This suggests a limited capacity of the $CeO_2(111)$ surface to interact with CO_2 molecules.

Electronic Structure. The charge transfer between CeO_2 surface and CO_2 adsorbates as a function of the coverage is depicted in Figure 7. When CO_2 is adsorbed as monodentate species the charge transferred per CeO_2 surface unit increases linearly with the coverage up to $1/3$ ML. At higher coverages, it shows a convex behavior converging towards ca. $0.18 e^-/CeO_2$ and demonstrating the limits of CeO_2 as e^- donor. Thus, at coverages $>1/3$ ML, the CeO_2 substrate is no longer capable to donate the optimal amount of electrons to each adsorbed CO_2 species which contribute to the occupation of LUMO of the unbound species (Figure 3b), resulting in a loss of bond strength (Figure 5a). It is suggested that interactions between CO_2 adsorbates influence the capacity of each single CO_2 to uptake electrons and thus also contribute to a limited charge transfer. This is further supported by the behavior of bidentate species. At low coverage ($1/9$ ML), basically the same charge is transferred to mono- and bidentate species. However, the convex behavior of the charge transfer already at low coverages causes the curve of bidentate

species to lie below the one of monodentate species. Moreover, the charge transfer to bidentate species converges to $0.13 \text{ e}^-/\text{CeO}_2$ at higher coverages which is about $0.05 \text{ e}^-/\text{CeO}_2$ lower compared to monodentate species.

In summary, a CO_2 molecule adsorbed in a bent configuration (mono- and bidentate) acts as Lewis acid accepting electronic charge from the surface at all coverages. The limitation of charge transfer given by the value at the convergence at high coverage can act as an analyzer of the degree of basicity of the CeO_2 surface. In contrast, for linear adsorption, minor charge transfer (0.009 ± 0.005) is observed from the CO_2 molecule towards the CeO_2 surface. In this case, the surface acts as a weak acid.

Mixed Adsorption Mechanisms at High Coverage ($>1/4 \text{ ML}$). *Stability.* In addition to the simulations where all CO_2 are adsorbed in the same configuration, calculations are performed at coverages $>1/4 \text{ ML}$ for mixed adsorption mechanisms where different configurations of CO_2 exist at the same time. At $1/4$, $1/2$ and $2/3 \text{ ML}$ coverage, mixed configurations with monodentate and either linear (mono+lin) or bidentate (mono+bi) species are simulated. At 1 ML , additional configurations are investigated with all three adsorption configurations present simultaneously. The average binding energy for both types of mixed configurations at $1/4 \text{ ML}$ shows a linear behavior with increasing fraction of CO_2 adsorbed as monodentate species (Figure 8a). In fact, the pure monodentate adsorption is found to be the most stable configuration at $1/4 \text{ ML}$. The linear decrease in binding energy (increase in bond strength) with increasing amount of monodentate species evidences unperturbed superposition of the binding energies of single-phase configurations (monodentate ratio equal to 0 or 1) indicating negligible interactions between adsorbates.

A similar behavior is observed at 1/2 ML coverage in the mono+bi configuration (Figure 8b, triangles). In contrast, in the mono+lin (Figure 8b, circles) configuration, the bond strength is maximal (minimum in E_B) when 2/3 of the CO₂ molecules are adsorbed in a monodentate configuration, having a binding energy of -0.17 eV. This ratio of monodentate species corresponds to a coverage of 1/3 ML. This is identical to what is found at 2/3 and 1 ML for the mixed configurations: the bond strength is maximal for a fraction of monodentate species of 1/2 and 1/3, respectively. Again, in both cases, this fraction corresponds to a total of 1/3 ML of monodentate species. At 1 ML, additional configurations are calculated at the minimum, where 1/3 ML monodentate species are adsorbed together with both bidentate and linear species. The coverage of bidentate species in these configurations is 1/9, 1/4 and 1/3 ML. The highest value of E_B (least stable) is found at 1/3 ML bidentate and it decreases monotonously with decreasing amount of bidentate species.

In summary, at all investigated coverages a configuration with 1/3 ML monodentate species and additional linear adsorption is most stable. This suggests that CO₂ initially binds as monodentate carbonate to the CeO₂(111) surface up to 1/3 ML and further CO₂ adsorption results in the formation of linear species.

Geometry. Geometry of mixed adsorption mechanisms will be discussed here only for the most stable configurations. These are the mixed configurations where 1/3 ML is adsorbed as monodentate carbonate and additional CO₂ is adsorbed linearly (Table 3). For completeness, results for the configuration with monodentate and linear species at 1/4 ML total coverage are reported as well in Table 3.

The C-O bond length (d_{C-O} , Figure 1) is significantly larger in the monodentate (1.27 Å) than the linear (1.17 Å) species at all coverages, similar to the results for homogenous adsorption

mechanisms. It is independent of the total CO₂ coverage demonstrating that the monodentate species remain in an activated conformation upon further adsorption of linear CO₂ species. Linear species adsorb at different heights depending on the coverage. Linearly adsorbed CO₂ molecules in the first partial layer (1/3 ML) align along the $[11\bar{2}]$ direction in between the monodentate species (Figure 6f) and are in average $\Delta z_{\text{CO}_2} \approx 4$ Å above the surface. Starting the optimization from different initial configurations of the first partial layer of linear CO₂ always results in this configuration demonstrating attractive interactions with the monodentate species. Additional CO₂ molecules adsorb at ca. 5 Å above the surface.

As discussed above, the $d_{\text{C-O}_{\text{surf}}}$ distance for homogenous adsorption of monodentate species remarkably increases from 1.38 to 1.41 Å with increasing coverage from 1/3 to 2/3 ML (Figure 5b). In contrast, for a mixed adsorption of monodentate and linear species, it remains constant at 1.38 Å. This again indicates that the additional linear molecules do not affect the configuration of the chemisorbed monodentate species.

Electronic Structure. As discussed above, the average charge of a CO₂ molecule in the monodentate configuration increases steadily with increasing coverage. In contrast, in the mixed mono+lin configuration, the average charge CO₂ in a monodentate configuration decreases slightly when linear species are additionally adsorbed (Figure S74) at a total coverage >1/3 ML. This is accompanied by a marginal increase in charge of the linear CO₂ species and indicates a charge transfer from the linear to the monodentate species.

Figure 9 shows the PDOS on the orbitals of the different CO₂ species observed in the most stable mixed (mono+lin) configuration at 1 ML (Figure 6c,f) where 1/3 ML is adsorbed as monodentate species and two partial layers of linear CO₂ can be distinguished. The orbitals of monodentate CO₂ lie at the same energy as the ones for the isolated monodentate configuration

(Figure 2). On the other hand, the DOS of the two different linear species shows the characteristic bands of the gas phase CO₂ molecule. Interestingly, the bands of the linear CO₂ molecules closer to the surface are shifted to slightly lower energies compared to the more distant CO₂ species by ca. 0.4 eV. This demonstrates a stabilization of the first partial layer of linearly adsorbed CO₂ molecules due to the pre-adsorption of monodentate carbonate species and is confirmed by the charge transfer from linear CO₂ to the bent species and the alignment of the linear species in their geometry [11 $\bar{2}$] (Figure 4f).

CONCLUSIONS

Adsorption properties of CO₂ on a CeO₂(111) surface have been investigated with standard DFT calculations using the PBE exchange-correlation functional. Three stable configurations have been distinguished of isolated CO₂ (1/9 ML) species adsorbed on the CeO₂ surface: (i) monodentate carbonate, (ii) bidentate carbonate and (iii) linear species. In both carbonate configurations the CO₂ molecule is bent with the C atom forming a chemical bond to a surface O atom. The chemical bond formation has been confirmed by the change of geometry of the CO₂ molecule and the hybridization of its orbitals with the orbitals of the surface O. Analysis of the PDOS and the differential charge distribution suggest the occupation of the LUMO of a bent CO₂ in gas phase upon adsorption. In contrast to the bent configurations, the linear species is physisorbed. Geometry and electronic structure of the latter have been found to be identical to the ones of a gas phase CO₂. Among these three configurations, the most stable one is the monodentate species with a binding energy of -0.31 eV.

Upon formation of monodentate carbonate, the C-O bond elongates to 1.27 Å. This bond length is comparable to the one found for bent CO₂ on several metal surface such as Rh, Pd and Pt, indicating a similar CO₂ activation. A charge transfer of 0.46 e⁻ has been observed from the CeO₂(111) to the monodentate CO₂ species demonstrating the basic character of the CeO₂(111) surface. It is in contrast to what has been observed on some other metal oxides such as TiO₂⁵⁶ where linear adsorption was favored.

The coverage effect has been investigated for the three stable configurations. It has been observed that the bond strength of both monodentate and bidentate species decreases with increasing coverage of CO₂, which can be attributed to the restricted charge transfer capacity of the CeO₂ substrate. This leads to a drastic loss of bond strength at coverages >1/3 ML. It has

been observed that the limit for electron donation per CeO_2 surface unit from the substrate to the adsorbate is lower for bidentate than for monodentate species.

Furthermore, mixed configurations have been investigated at coverages $>1/4$ ML where monodentate and either bidentate or linear species are adsorbed simultaneously. At 1 ML, additional tri-structural configurations have been examined where mono-, bidentate and linear species are present at the same time. It has been observed that mixed configurations with monodentate and linear species are most stable at all coverages. Different fractions of monodentate species have been simulated yielding a minimum of the binding energy when an absolute amount of $1/3$ ML of monodentate species is present on the surface.

These results lead us to the conclusion that CO_2 adsorbs as monodentate carbonate on the $\text{CeO}_2(111)$ surface up to a coverage of $1/3$ ML. At higher coverages, mixed CO_2 configurations are formed where multilayers of linear species adsorb above the monodentate species. The binding energy of such configurations has been shown to increase marginally to -0.11 eV at 1 ML. Analysis of the density of states has revealed that the first partial layer of linear CO_2 is stabilized by the pre-adsorbed monodentate species.

This study provides fundamental insight of the adsorption properties of CO_2 on $\text{CeO}_2(111)$ demonstrating that $\text{CeO}_2(111)$ is capable of activating CO_2 up to a certain coverage ($1/3$ ML). It is a basis for further investigation of CO_2 reaction mechanisms with hydrogen on CeO_2 -based catalytic surfaces. Furthermore, dynamic studies, such as molecular dynamics or meta-dynamic simulations, are planned to be directly compared to experimental results of IR-spectroscopy at finite temperatures and pressure³¹. These are expected to give a more realistic picture of the different adsorption mechanisms and properties of mixed adsorption at specific process parameters.

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SUPPORTING INFORMATION

Supporting information contains the binding energies of CO₂ on CeO₂(111) for selected configurations calculated with the PBE0 method, the PDOS on s-, p- and d-type orbitals of CO₂ and O_{surf} of the monodentate species, the PDOS of mono-, bidentate and linear species and the average charge per CO₂ molecule as a function of the coverage.

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Table 1. Lattice parameter a of CeO₂ bulk and surface energy E_{surf} of its stoichiometric (111) surface calculated with different methods and compared to literature values.

Method	a [Å]	E_{surf} [J/m ²]	reference
PBE	5.48	0.74	this work
PBE0(20%)	5.44	0.78	this work
PBE	5.47	0.68	Ref ³⁸
PBE+U	5.48	0.72	Ref ⁵¹
LDA+U	5.38	1.02	Ref ⁵¹
exp	5.41		Ref ⁵⁰

Table 2. Binding energy (E_B), geometric properties (explained in Figure 1) and total charge of CO_2 in the gas phase and adsorbed in different single-phase configurations on the $\text{CeO}_2(111)$ surface at 1/9, 1/2 and 2/3 ML coverage.

		E_B [eV]	$d_{\text{C-O1}}(d_{\text{C-O2}})$ [Å]	$d_{\text{C-Osurf}}$ [Å]	Δz_{CO_2} [Å]	α_{COC} [°]	charge
	gas phase	-	1.17	-	-	180.0	0.00
1/9 ML	monodentate	-0.31	1.27	1.38	-	129.7	-0.46
	<u>DFT+U</u>	<u>-0.28</u>	<u>1.27</u>	<u>1.38</u>	<u>-</u>	<u>129.5</u>	<u>-0.47</u>
	PBE0(20%)	-0.68	1.26	1.36	-	129.4	-0.54
	PBE0(20%) ^a	-0.65	1.26	1.36	-	129.4	-0.54
	bidentate	-0.12	1.22 (1.30)	1.41	-	129.2	-0.40
	<u>DFT+U</u>	<u>-0.04</u>	<u>1.22 (1.30)</u>	<u>1.43</u>	<u>-</u>	<u>130.3</u>	<u>-0.41</u>
	PBE0(20%) ^a	-0.42	1.21 (1.29)	1.40	-	129.7	-0.48
	linear	0.02	1.17	-	3.52	177.6	0.03
1/2 ML	monodentate	-0.08	1.26	1.40	-	131.8	-0.34
	bidentate	0.19	1.21 (1.30)	1.44	-	131.0	-0.26
	linear	0.00	1.17	-	3.43	177.8	0.03
2/3 ML	monodentate	0.36	1.25	1.41	-	131.4	-0.27
	bidentate	0.43	1.20 (1.29)	1.46	-	131.6	-0.19
	linear	0.03	1.17	-	3.92	178.6	0.01

^a spin-polarized calculations

Table 3. Binding energy (E_B), geometric properties (see Figure 1) and total charge of CO₂ molecules adsorbed in mixed configurations (mono+lin) on CeO₂(111) surface at different coverages.

coverage [ML]			E_B [eV]	d_{C-O} [Å]		α_{COC} [°]		charge	
total	mono	lin		mono	lin	mono	lin	mono	lin
1/4	1/8	1/8	-0.12	1.27	1.17	129.8	178.4	-0.45	0.04
1/2	1/3	1/6	-0.17	1.26	1.17	130.0	177.5	-0.43	0.06
2/3	1/3	1/3	-0.17	1.27	1.17	129.3	177.4	-0.48	0.06
1	1/3	2/3	-0.11	1.27	1.17	129.3	178.6	-0.50	0.03

FIGURE CAPTIONS

Figure 1. (a, b, c) Cross-sectional and (d, e f) top view of stable configurations of isolated CO₂ adsorbed on a CeO₂(111) surface. In the most stable configuration (a, d), CO₂ forms a monodentate carbonate with the surface O atom resulting in a binding energy of -0.31 eV. The binding energy of the bidentate and linear configurations was found to be -0.12 and +0.02 eV, respectively.

Figure 2. PDOS summed over all atoms (black) and on specific species (Ce_{slab}, O_{slab}, O_{surf} and CO₂) of isolated (1/9 ML) CO₂ adsorbed on CeO₂(111) in a monodentate configuration. The grey and red lines indicate the PDOS projected on the orbitals of Ce and O atoms, respectively, of the CeO₂ substrate. The orange line shows the PDOS on the orbitals of the surface O atom interacting with the CO₂ molecule (O_{surf}). The green line shows the PDOS on orbitals of the adsorbed CO₂ molecule. Filled curves indicate occupied orbitals and the reference 0 eV energy was set to the edge of the valence band of the CeO₂(111) slab. Upon adsorption, the HOMO of the CO₂ molecule forming a carbonate species with the O_{surf} atom, is found at 0.33 eV above the valence band of CeO₂(111).

Figure 3. (a) PDOS of linear CO₂ in gas phase, bent CO₂ in gas phase and projected DOS of CO₂ adsorbed on CeO₂(111) as mono- and bidentate species and (b) selected electronic states derived from the molecular orbitals of the CO₂ species. Upon adsorption, the LUMO (2) of gas phase CO₂ hybridizes and the binding orbital becomes occupied. Occupied molecular orbitals of both adsorbed species corresponding to the LUMO of the gas phase CO₂ were found in the valence band between ca. -2.5 and 0 eV (4, 6).

Figure 4. Charge density difference at $0.067 \text{ e}/\text{\AA}^3$ for (a) monodentate and (b) bidentate CO_2 species. Yellow lobes indicate electron excess and cyan lobes indicate loss of electron density. The excess of electrons between O_{surf} and C demonstrates the filling of the LUMO (see Figure 3) of gas phase CO_2 and the binding character between the two atoms.

Figure 5. (a) Binding energy E_B and (b) $d_{\text{C-O}_{\text{surf}}}$ distance as a function of the CO_2 coverage of linear (circles), bidentate (triangles) and monodentate (diamonds) species and for a mixed configuration (filled diamonds) with 1/3 ML monodentate species and additional linear CO_2 . At 1 ML, the most stable configuration consisted of 1/3 ML monodentate and 2/3 ML linear species.

Figure 6. (a, b, c) Cross-sectional and (d, e, f) top view of (a,d) monodentate species at 2/3 ML and (b,d) bidentate species and (c,f) a mixed configuration of monodentate and linear species at 1 ML. The two adjacent rows in $[01\bar{1}]$ direction of monodentate species at 2/3 ML in (d) share one surface Ce site ($\text{Ce}_{\text{surf},2}$) leading to a rotation of the CO_2 molecules away from this Ce atom. When CO_2 is adsorbed in a bidentate configuration at 1 ML, the molecules arranged in a zig-zag pattern (e). CO_2 molecules of the mixed configuration are represented with different green spheres to differentiate between various species. The first partial layer of linear CO_2 (green spheres) arranged in $[11\bar{2}]$ direction in between the monodentate species (dark green spheres) at $\Delta z_{\text{CO}_2}=3.84 \text{ \AA}$. Linear CO_2 adsorbed in a second partial layer (light green spheres) were found at $\Delta z_{\text{CO}_2}=5.01 \text{ \AA}$.

Figure 7. Charge transfer per surface CeO_2 unit from the surface to CO_2 adsorbates as a function of the CO_2 coverage for linear (circles), mono- (diamonds) and bidentate (triangles) species and for a mixed configuration (filled diamond) with monodentate and linear species.

Figure 8. Average binding energy of CO₂ adsorbed simultaneously in different configurations at a total CO₂ coverage θ of (a) 1/4, (b) 1/2, (c) 2/3 and (d) 1 ML. The binding energy is shown as a function of the fraction of CO₂ adsorbed as monodentate species at each specific total coverage. At $\theta > 1/2$ ML, the binding energy has minimum when 1/3 ML (green line) of CO₂ is adsorbed as monodentate species. Additional mixed configurations were simulated at 1 ML (d) where all mono-, bidentate and linear species were present. Here, the amount of monodentate species was fixed to 1/3 ML and the amount of bidentate species was varied from 1/9 to 1/3 ML. Nevertheless, the most stable state (lowest binding energy) was found when only monodentate (1/3 ML) and linear (2/3 ML) species existed.

Figure 9. PDOS for the mixed configuration with monodentate (1/3 ML) and linear (2/3 ML) species at 1 ML. The pDOS of monodentate CO₂ (dark green) was identical to the one of isolated species (Figure 2) whereas the linear CO₂ showed the same bands as the gas phase molecule (Figure 3). Molecular orbitals of linear CO₂ adsorbed in the first partial layer (linear low) were shifted by ca. 0.40 eV to lower energies compared to linear species in the second partial layer (linear high) indicating stabilization of the CO₂ molecules closer to the surface.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

FIGURE 9